PERFORMANCES OF METALLIC FOAMS AS SUPPORTS FOR CATALYSTS

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الملخص

تم دراسة نوعين من حشوات الرغوة (Foams fillers) المستخدمة في المفاعلات ومقارنتها بالأنواع التقليدية (Packed Bed)، بهدف معرفة كفاءة هذه الأنواع من ناحية انتقال المادة والتوصيل الحراري. تم في هذا العمل اختبار التفاعل الماص للحرارة وهو تحويل المثيل سيكلوهكسان إلى هيدروجين وتولوين باستعمال الحفاز (2% Pt/γ -Al_2O_3) لإنتاج الهيدروجين المستعمل في تطبيقات خلايا الوقود (Fuel cell) بهدف إنتاج الطاقة الكهربائية. من خلال النتائج المتحصل عليها في هذه الدراسة وجد أن الأنواع الجديدة لها توصيلية أكبر من الأنواع التقليدية مما يجعل منها بديل أفضل لأن المقاومة لعملية التوصيل الحراري تكون أقل للتفاعلات الماصة للحرارة . كما تبين من النتائج الخاصة بقياسات الانخفاض في الضغط أن هذه الأنواع الجديدة من الحشوات يكون فيها معدل انخفاض الضغط ($\Delta P_{\text{with cata}} = 476$ Pa.m^{-1} at $u = 0.92$ m.s^{-1}) أقل بكثير مقارنة بالحشوات التقليدية ($\Delta P_{\text{with cata}} = 1600$ Pa.m^{-1} at $u = 0.92$ m.s^{-1}). وهذا يعنى أن كمية الطاقة المطلوبة تكون أقل.

ABSTRACT

Two types of catalytic foams-filled metallic and ceramic reactors having different pore sizes were investigated and compared with fixed bed reactors in order to observe the thermal effects and try to identify the key parameters that promote both heat and mass transfer. The performance of foam-filled reactor with conventional fixed bed reactor was examined using an endothermic reaction. The reaction was the dehydrogenation of mehtylcyclohexan (MCH) to toluene on 2% Pt/γ -Al_2O_3, which is considered to be suitable reaction used to produce hydrogen for fuel-cell application. It was found that, for endothermic reactions not limited by external transport, the coated foams significantly increased the effective conductivity of catalytic beds, the denser foam leading to higher effective conductivity. The results indicate a much higher pressure drop of the beads ($\Delta P_{\text{with cata}} = 1600$ Pa.m^{-1} at $u = 0.92$ m.s^{-1}) compared to that of the different foams ($\Delta P_{\text{with cata}} = 476$ Pa.m^{-1} at $u = 0.92$ m.s^{-1}), and the Innocenti et al. correlation agrees very well with experimental data compared with other correlations

KEYWORDS: Foams; Packed Bed; Catalyst; Supporters; Pressure drop.

INTRODUCTION

The metal foam has potential advantages as substrates catalyst support in heterogeneous fixed bed reactors and they have been subject of significant attention in the chemical process industry. Many important reactions in chemical industry, such as hydrocarbon dehydrogenation and methane steam reforming for syngas or hydrogen

production, are endothermic and require high process temperature. The high porosity and tortuosity of the metal foam support enhances the turbulence, mixing and transport of fluids through the support. This results in significant advantages due to the use of metal foam supported catalysts for certain catalytic processes, especially those processes which would otherwise be limited by mass transfer or heat transfer. Additionally, the improved mixing can increase reaction rates, reaction yields, and reduce contact times. The high porosity of metal foam supports results in a lower pressure drop, particularly when compared with beds that are packed with small particles. In certain embodiments, the pressure drop is at least 3 times less than that with a packed bed. The metallic catalyst supports have superior thermal and mechanical properties over ceramic supports. Consequently, metallic supports have gained considerable attention in the past decade [1, 2]. The catalysts coating onto metal foam supports such as wash coating, sol–gel, wetness impregnation have been reported by Meille [3].

Do Hyung Kim [4] investigated the adhesion properties of washcoated γ-Al_2O_3 layer on FeCrAl metal foams, they found the weight gain after washcoating was 19–20 wt.% for FeCrAl foam even without preoxidation and it was much higher than that on planar FeCrAl foil with preoxidation. The heat transfer in metal foams in commercial filled tubular reactors has been studied by C. Hutter [5]; they presented the metal foam reactors and have highlighted their potential use for continuous chemical production, and they found that the heat transfer increased with the ligament diameter ascribed to the enhanced turbulent kinetic energy induced. A strong impact on mass transfer was observed in the investigation of Hutter [6], wherein the mixing efficiency of metal foam was found to be comparable to commercial static mixing elements. C. Hutter [7] investigated the axial dispersion in metal foams and laser sintered reactors on available metal foams of 20 and 30 ppi, their results showed that the high potential of foam reactors for catalyst driven reactions. They provide the same or even a higher surface area per volume of catalyst bed while inducing a much smaller pressure drop than corresponding fixed beds.

While the pressure drop in foams (ceramic or metallic) has been extensively studied in the literature [8-13], Devid [10] summarizes most of commonly used correlations for different geometry. The main problem appears today to validate these correlation as a function of geometry parameters of the used foams ; i.e , is the modul capable of representing the exact shape (Cubic cell, Dodecahedron, Tetrakaidecahedron) to give important information on the three essential parameters (strut diameter d_s, specific area a_c, porosity ε). Morphology study can be used to characterize the struts diameter, pores size and the foams porosity.

In this work, the effect of the foam catalyst loading on the pressure drop has been examined. The effect of the foam nature and density on the temperature profile in the reactor has also been studied using an endothermic model reaction. Heat characteristics parameters used were based on the commercially available metal foams. Commercial FeCr Alloy foams with pore sizes of 20 and 30 ppi (pore per inch) were applied with gravimetrically estimated porosities of 95% and 90%.

EXPERIMENTAL SETUP

Catalytic foams and bead preparation

The foam sheet (1.2 cm thick) was cut into rectangular pieces of 4.9 × 19 cm. The pieces were washed with acetone and then calcined at 500°C to ensure a clean surface

prior to coating. The catalyst (2% Pt/Al_2O_3) was deposited on the metallic and ceramic foams by dip-coating as shown in Figure (1). The suspension contained the catalyst powder, water and nitric acid. After evacuation of excess suspension, the coated foams were dried at room temperature and calcined at 500°C. Zeolite beads were covered by the active layer by dry impregnation with the same suspension. All the coated samples are gathered in Table (1).

Figure 1: Coated foam and beads

Table 1: The four structures used in this work (in bold, catalyst mass used in catalytic tests)

Foam type	*Structure*	*Size*	*Porosity*	m_{cata} *(g) in 19cm long*
F1	FeCrAlY foam	33 ppi	97%	0 – **2.6** – 6.1
F2	FeCrAlY foam	33 ppi	81%	**2**
F3	Al_2O_3 foam	37 ppi	87%	**2.65**
B	Zeolite beads	2 mm diam.	40%	**2.55**

Pressure drop

The pressure drop was measured using the apparatus schematized in Figure (2). The box consists in two Plexiglas plates of internal dimensions: 4.9 cm × 39 cm × 1.2 cm. The foams structure was wrapped with a thin layer of Parafilm to prevent flow bypass. Gas flow rate was measured with BROOKS mass flow rate controller, and due to small pressure drops expected in the foams, a specific liquid barometers was used. Pressure drop was measured through 15 cm long, varying the gas velocity in the 0-1 $m.s^{-1}$ range.

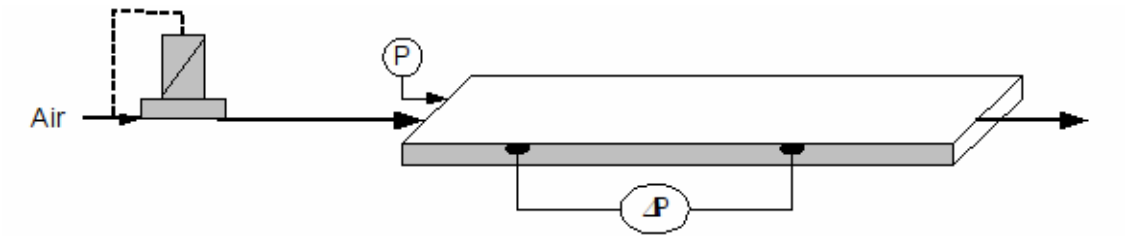

Figure 2: Pressure drop device.

The correlations for the pressure drop in foams based on bed properties [9]. The mean value of d_p (foam pore diameter (m)) was found from an imaging technique, and a simple hydraulic diameter model used which relates S_v (external surface area per volume of solid (m^2 m (solid)$^{-3}$) to d_p and the porosity, ε, and gives essentially identical results as those from more complex geometric models. Pressure drop versus velocity data followed the Forscheimer equation was interpreted with the conventional Ergun model [14]:

$$\frac{\Delta P}{L} = \frac{\alpha S_V^2 \mu (1-\varepsilon)^2}{\varepsilon^3} V + \frac{\beta S_V \rho (1-\varepsilon)}{\varepsilon^3} V^2 \quad , S_V = \frac{4\varepsilon}{d_p (1-\varepsilon)} \tag{1}$$

Where μ is the fluid viscosity, ρ the fluid density, V the superficial fluid velocity and α and β are the Ergun parameters, usually assumed to be constant. However, α and β are not constant but depend on the properties of the foam. Empirical relationships for α and β in terms of the mean pore diameter and the foam porosity were found and used to predicted pressure drop within ±15% for 10–65 ppi foams.

Catalytic test (Dehydrogenation of MCH)

Catalytic tests were performed in a stainless steel rectangular reactor of internal dimensions: 4.9 cm × 39 cm × 1.2 cm. The reactor was composed of two zones – the first zone was filled with a non reactive foam used to homogenize the gas flow rate, while the second zone was filled with a catalytic packing (Dimensions: 4.9 cm × 39 cm × 1.2 cm) (foam or beads). The reactor was equipped with specific graphite gasket (DELTGRAP HT) designed to resist to high temperatures as shown in Figure (3).

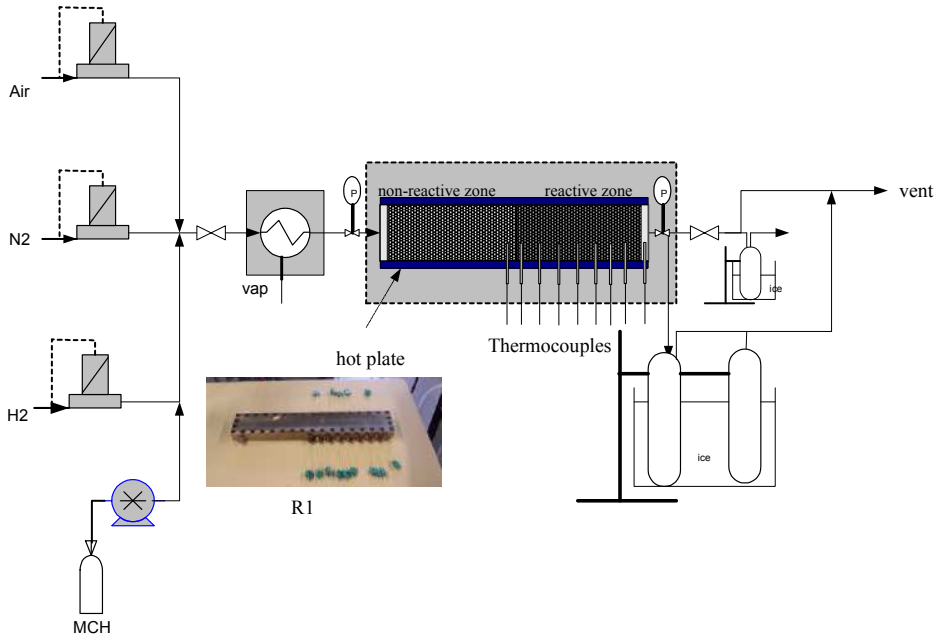

Figure 3: Experimental setup used for catalyst testing

The dehydrogenation of methylcyclohexane (MCH) was carried out in this reactor. This endothermic reaction yields toluene (TOL) and hydrogen (H_2), which not limited either by external mass transport or by internal mass transport. Every structure

was coated with c.a. 2.5 g catalyst (Table 1). The MCH flow rate was maintained with a ISMATEC pump in the range 1 to 9 $g.min^{-1}$. The reactor was heated with two hotplates fixed at top and bottom of the reactor and the temperature is regulated by a thermocouple inserted in the catalytic foam (6 cm from the beginning). The effluent of the reactor was condensed by two condensers at 0°C, and the sample was analyzed by GC. Experiments were performed at the same residence time for each structure by adjusting the inlet volume flow rates of MCH and H_2.

RESULTS AND DISCUSSION

Pressure drop

Three different catalyst loadings of foam (F1) were studied. There is a very slight effect of the loading on pressure drop (Figure 4-a). The results present the pressure drop in ceramic foams is higher than metallic foams, these results is in good agreement with those reported by David et al [10]. Concerning the structure nature, the results shown in Figure (4-b) indicate a much higher pressure drop of the beads ($\Delta P_{\text{with cata}}$= 1600 $Pa.m^{-1}$ at u = 0.92 $m.s^{-1}$) compared to that of the different foams ($\Delta P_{\text{with cata}}$= 476 $Pa.m^{-1}$ at u = 0.92 $m.s^{-1}$). Evidently, among the three different foams, that with the lowest porosity presents the highest pressure drop.

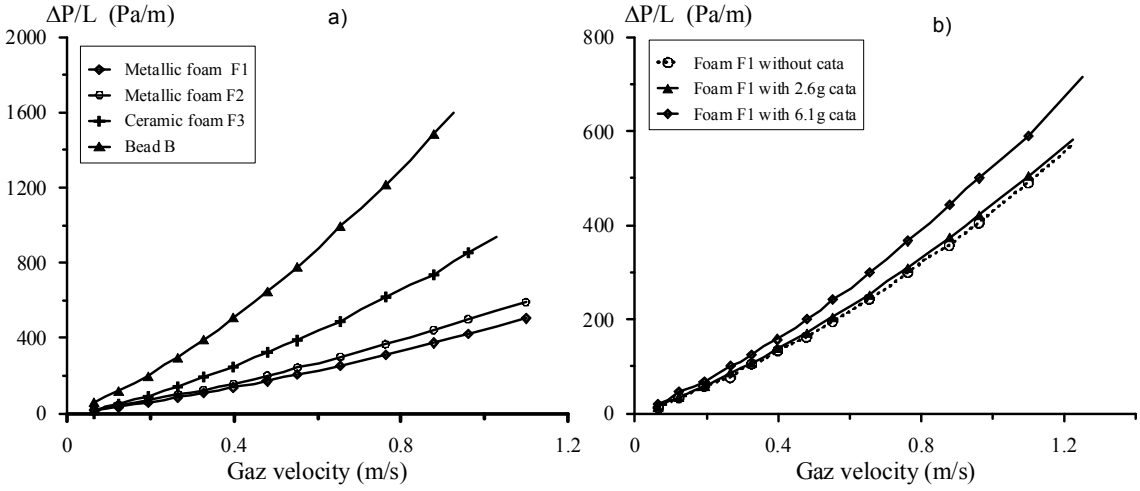

Figure 4: Comparison of pressure drops foams and bead with and without catalyst. (a) Effect of catalyst loading. (b) Effect of structures

As mentioned previously in the literature [10], the major problem to estimate the foams pressure drop is to define the structure properties of the matrix foams. Figure (5) presents the foams pressure drop by several correlations compared with our measured foams pressure drop in three types of foams (one ceramic and two metallic). The results show that the measured foams pressure drop was found in the range of these correlations. The discrepancy in the estimated pressure drop is attributed to the inaccuracy in the geometrical model structure proposed which is based on only three parameters to estimate the strut diameters and foams matrix. Table (2) present the comparison between the estimated values of dp with measured values for different models.

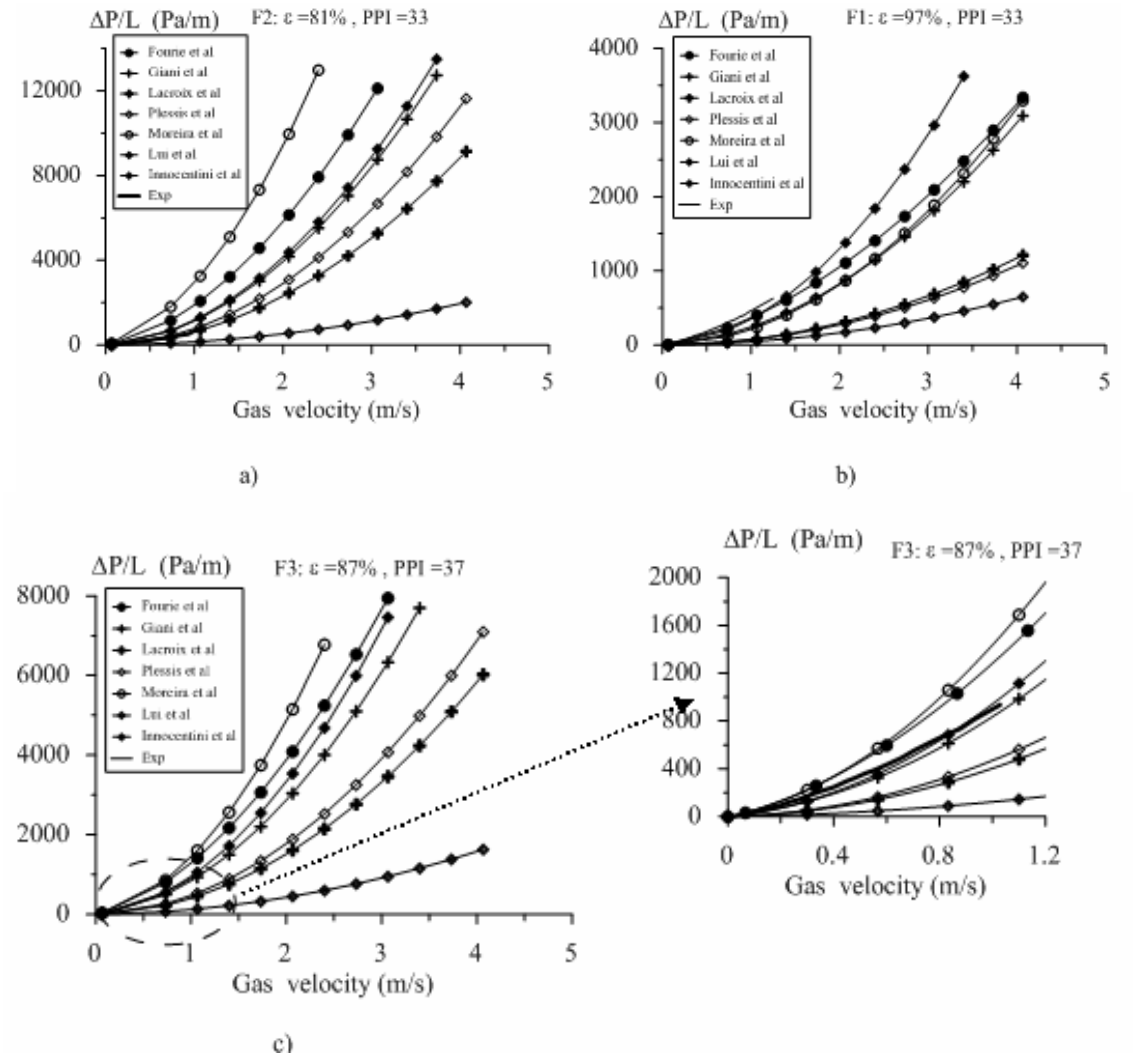

Figure 5: Comparison of pressure drop results determined by different models with experimental data: a) F2: ε =87% , ppi =33, b) F1: ε =97% , ppi =33, c) F3: ε =87%, ppi =37

Table 2: Comparison between the estimated values using different models with measured values of dp

Foam characteristics	Calculated d_p (mm) metallic ε =97%	Calculated d_p (mm) metallic ε =81%	Calculated d_p (mm) ceramic ε =87%
Lacroix [13]	0.626	0.933	0.776
Giani [14]	0.555	0.593	0.593
Plessis[8]	0.569	0.910	0.737
Fourie [8]	0.569	0.910	0.737
measured value	0.11 to 0.20	(0.25 to 0.646)	(0.19 to 0.38)

Finally, the correlations presented in the literature cannot give an exact value of pressure drop (these correlations are based on different parameters [a, d_p, ε, tortuosity]; type of material; geometrical model). These results agree with the conclusion found by David [10] that no perfect model can be used to estimate the foams pressure drop.

Catalyst tests

The effect of the structure nature on the temperature gradient in the reactor was studied using MCH dehydrogenation reaction as a model. First of all, it was checked that, without reaction a flat temperature profile was observed for all structures as shown in Figure (6). The results present very low effect of gas temperature due to low gas flow rates under reaction conditions.

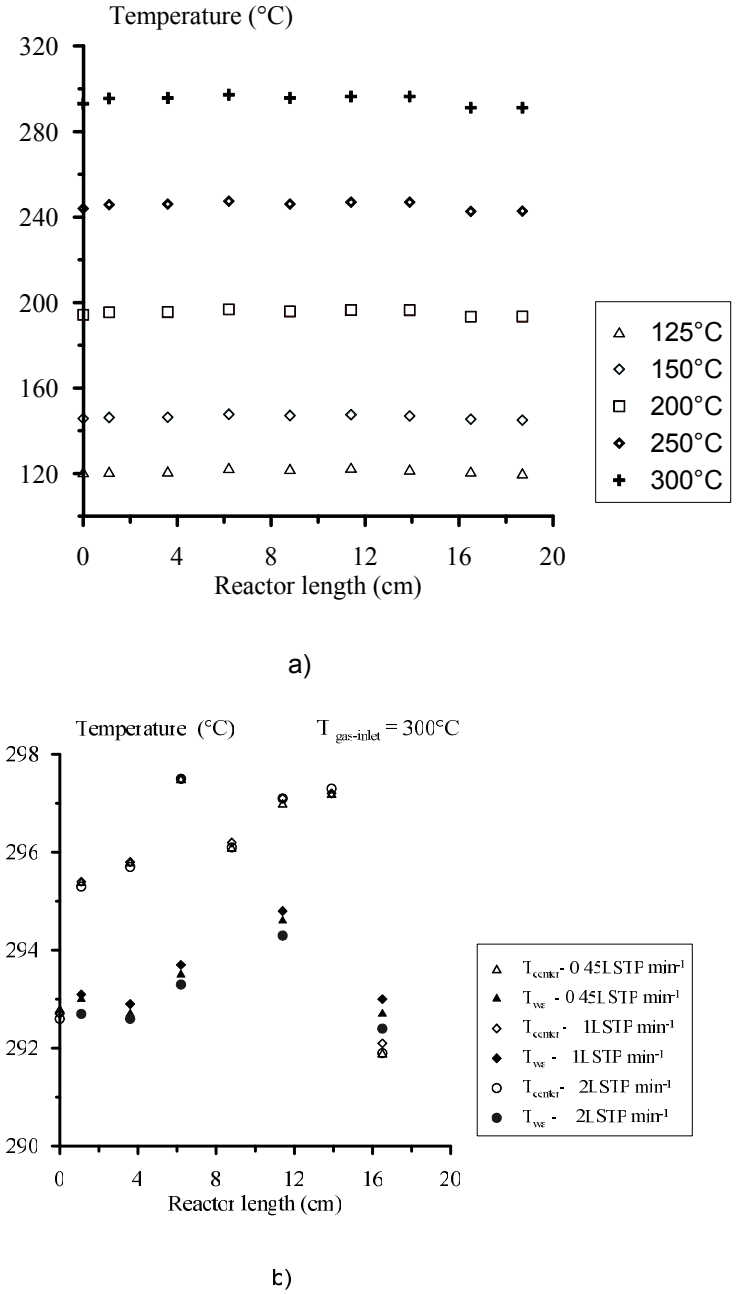

Figure 6: Temperature profile in the reactor: a) pure conduction with no gas convection, b) conduction and convection with pure gas

Then, the four different types of packing were studied in the reactive zone to observe the thermal effects to identify one key parameter that can improve the heat transfer. Figure (7) presents the results for center and wall temperature profiles of the

four structures at inlet gas temperature of 300°C, and at W/F_{MCH} of 15.3 $kg_{cata}.s.mol^{-1}$. It should be noticed that the temperature range is not the same for all structures, due to the position of the regulation thermocouple (6 cm from the beginning of the structure at half-thickness). This affects also MCH conversions that cannot be easily compared (Table 3). However, the comparison of thermal gradients at the same conversion for several structures highlights the behavior of these structures to improve heat transfer. The maximal temperature gradient between center and wall is presented in Figure (7).

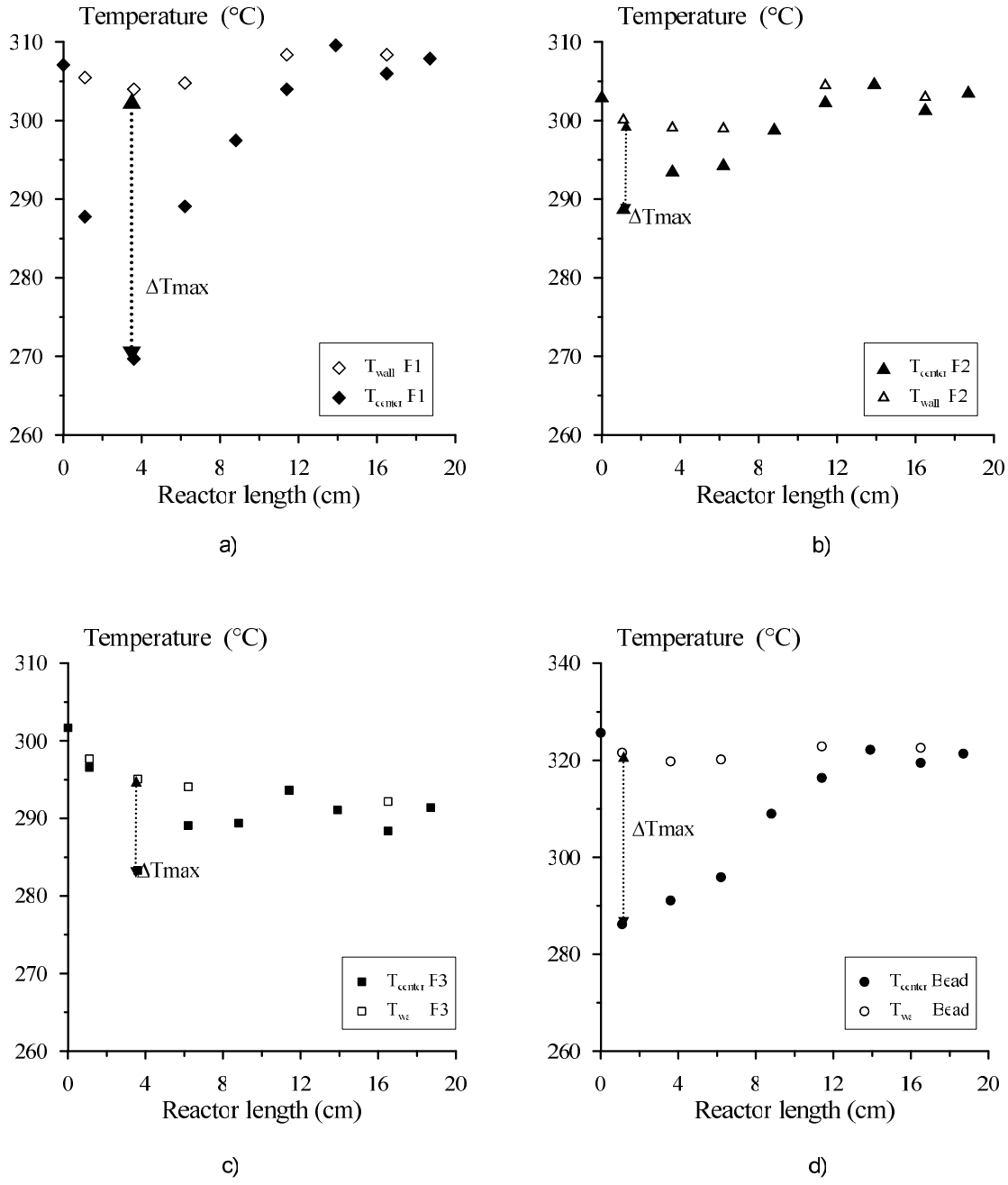

Figure 7: Axial temperature profile for foams types and bead bed reactor at W/F_{MCH} of $15.3kg_{cata}.s.mol^{-1}$ and at T_f=300°C: a) Foam F1, b) Foam F2 , c) Foam F3 , d) Bead B.

The foams have higher effective conductivity than beads, i.e. ΔT_{max} is the highest in the beads. Moreover, a foam with low density (F1) presents a small thermal conductivity, comparatively to other foams (F2 and F3). Table (3) summarizes, for all the tests performed with the four structures at different operating conditions, the maximal thermal gradients (represented by the arrows on Figure 7). The best structure to avoid high temperature gradient and to approach an isothermal behavior is the denser metallic foam (F2).

Table 3: Maximal thermal gradients (ΔTmax) and MCH conversion.

	F1 : Metallic 33 ppi ε=97%		*F2 : Metallic 33 ppi ε=81%*		*F3 : Ceramic 37 ppi ε=87%*		*B : Molecular sieves Bead : 2mm*	
$W/F_{MCH}=15.3kg_{cata}.s.mol^{-1}$ $Q_{H2}=3.3\cdot10^{-4}mol.s^{-1}$ $T_{controler}=300°C$	ΔT°C	X	ΔT°C	X	ΔT°C	X	ΔT°C	X
	36	97	8	95	12	77	35	96
$W/F_{MCH}=30.6kg_{cata}.s.mol^{-1}$ $Q_{H2}=3.3\cdot10^{-4}mol.s^{-1}$ $T_{controler}=300°C$	40	88	11	87	19	74	49	91
$W/F_{MCH}=61.2kg_{cata}.s.mol^{-1}$ $Q_{H2}=7.4\cdot10^{-4}mol.s^{-1}$ $T_{controler}=300°C$	38	58	19	77	22	54	64	75
$W/F_{MCH}=91.8kg_{cata}.s.mol^{-1}$ $Q_{H2}=3.3\cdot10^{-4}mol.s^{-1}$ $T_{controler}=300°C$	43	40	21	53	26	36	64	53
$W/F_{MCH}=61.2kg_{cata}.s.mol^{-1}$ $Q_{H2}=7.4\cdot10^{-4}mol.s^{-1}$ $T_{controler}=325°C$	60	84	26	90	33	71	94	85
$W/F_{MCH}=91.8kg_{cata}.s.mol^{-1}$ $Q_{H2}=3.3\cdot10^{-4}mol.s^{-1}$ $T_{controler}=325°C$			33	68	35	57	99	62

CONCLUSION

Commercially available metal foams of three different porosities were investigated and compared with bead in a rectangle reactor to identify one key parameter that can improve the heat transfer. The reaction was the endothermic dehydrogenation of methylcyclohexane on 2%Pt/Al_2O_3 directly coated on foams and on molecular sieve beads. To study the influence of heat and mass transfers, the material (FeCr Alloy or alumina) and porosity (81–97%) of foams were varied. It was found that the reactions are not limited by external transport, the coated foams significantly increased the effective conductivity of catalytic beds, the denser foam leading to higher effective conductivity. The foams were coated with up to 100 $kg_{cata}m^{-3}$ without any significant increase in pressure drop.

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